

US009771459B2

US 9,771,459 B2

*Sep. 26, 2017

(12) United States Patent

Mittal et al.

(10) Patent No.:

(56)

(45) Date of Patent:

(54) CURABLE SILOXANE COMPOSITIONS

(71) Applicant: Momentive Performance Materials Inc., Waterford, NY (US)

(72) Inventors: Anuj Mittal, Bangalore (IN);

Raveendra Mathad, Bangalore (IN); Sumi Dinkar, Bangalore (IN);

Indumathi Ramakrishnan, Bangalore (IN); Manav Gupta, Bangalore (IN)

(73) Assignee: Momentive Performance Materials

Inc., Waterford, NY (US)

(*) Notice: Subject to any disclaimer, the term of this

patent is extended or adjusted under 35

U.S.C. 154(b) by 0 days.

This patent is subject to a terminal dis-

claimer.

(21) Appl. No.: 15/052,156

(22) Filed: Feb. 24, 2016

(65) Prior Publication Data

US 2016/0244571 A1 Aug. 25, 2016

Related U.S. Application Data

(60) Provisional application No. 62/120,540, filed on Feb. 25, 2015.

(51) **Int. Cl.**

C08F 2/46	(2006.01)
C08G 61/04	(2006.01)
C08G 77/50	(2006.01)
C08K 3/00	(2006.01)
C08K 5/00	(2006.01)
C09J 183/14	(2006.01)
C09D 183/14	(2006.01)
C09D 183/04	(2006.01)
C08L 83/14	(2006.01)
C08G 77/12	(2006.01)
C08G 77/20	(2006.01)

(52) **U.S. Cl.**

(58) Field of Classification Search

None

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS

3,220,972	\mathbf{A}	11/1965	Lamoreaux	
3,445,389	A *	5/1969	McKellar	C08G 77/00
				508/208
3,715,334	\mathbf{A}	2/1973	Karstedt	
3,775,452	\mathbf{A}	11/1973	Karstedt	
3,814,730	\mathbf{A}	6/1974	Karstedt	
5,386,007	\mathbf{A}	1/1995	Herzig et al.	
9,334,372	B1 *	5/2016	Mittal	C08G 77/448

FOREIGN PATENT DOCUMENTS

EP	0641819	9/1994
JP	2006-206884	* 8/2006
WO	9842789	10/1998

OTHER PUBLICATIONS

Hori, JP 2006-206884 Machine Translation, Aug. 10, 2006.* Putzien et al, UV Curing of Epoxy Functional Hybrid Silicones, Apr. 27, 2012, Journal of Applied Polymer Science, vol. 126, 1188-1197.*

J.L. Spier, Homogeneous Catalysis of Hydrosilation by Transition Metals, Advances in Organometallic Chemistry, vol. 17, pp. 407-447.

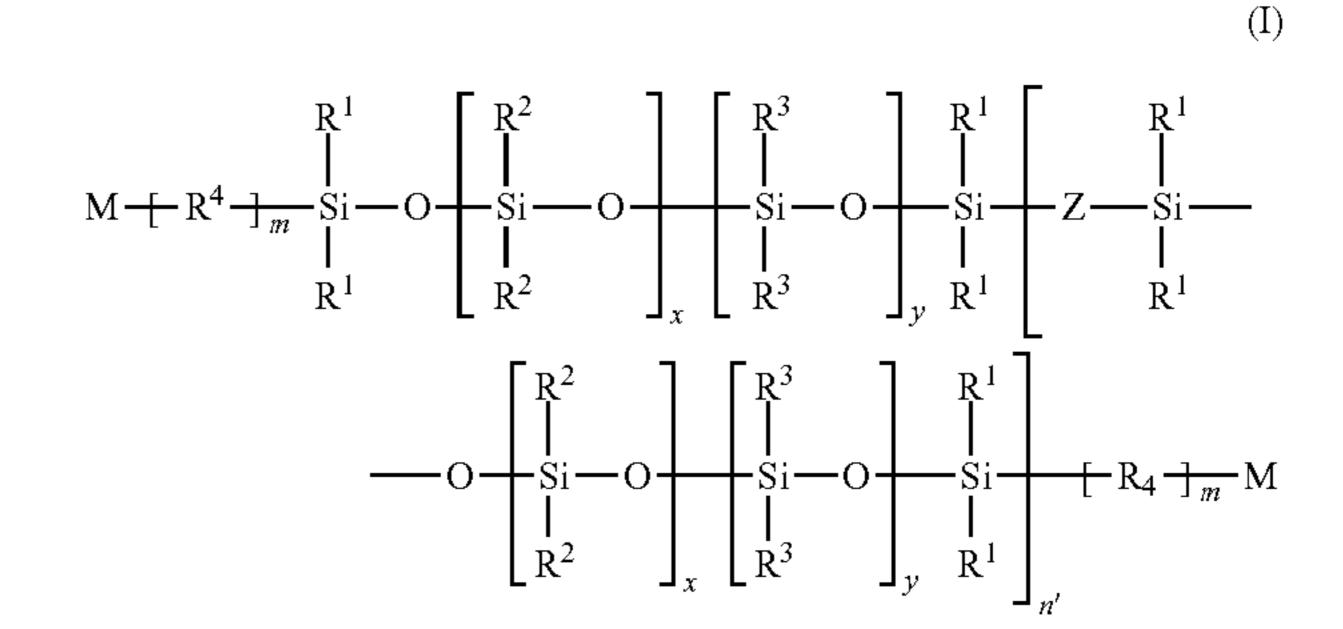
Written Opinion and Search Report from PCT/US2016/019287 dated Jul. 6, 2016.

* cited by examiner

Primary Examiner — Jessica E Whiteley (74) Attorney, Agent, or Firm — James C. Abruzzo

(57) ABSTRACT

There is provided herein a curable polysiloxane composition comprising a reactive polysiloxane having the general structural formula (I):



as described herein. There is provided a method of making the polysiloxane. In addition there is provided a curable composition including the polysiloxane.

24 Claims, No Drawings

FIELD OF THE INVENTION

The invention is directed to polysiloxanes, more specifi- 10 cally, reactive polysiloxanes and their use in curable compositions and applications containing the same.

BACKGROUND OF THE INVENTION

Polysiloxanes are well-known materials which have long been used as a reactive component to react or crosslink or cure with other materials in order to form a cured composition containing polysiloxane components. Cured compositions containing polysiloxane components are used in a 20 variety of applications. However, when these polysiloxane components are used, they often experience poor compatibility with the other components, resulting in poor clarity (haze), which is especially detrimental when clear compositions are desirable.

While reactive polysiloxanes have been prepared, many contain polysiloxane chains of dimethylsiloxy repeat units which make the polysiloxane incompatible with other organic polymers or other components in the composition. The polysiloxanes often result in poor paintability, due to the $_{30}$ chains of dimethylsiloxy repeat units. Reactive polysiloxanes have been prepared with pended groups to improve the compatibility with other components, such as pendent poly (aikyiene oxide) groups. However, these pendent groups often change the partial molar volume of the reactive 35 polysiloxane, resulting in a loss of physical properties, such as comparative tracking index, tensile, modulus and/or low temperature impact resistance. Therefore, there is a need for a reactive polysiloxane that improves the capability of the reactive polysiloxanes with other components of the composition, as determined for example by haze, without loss of the other physical properties.

SUMMARY OF THE INVENTION

In one non-limiting embodiment herein there is provided a polysiloxane having the general structural formula (I):

atoms, an unsubstituted or substituted acyl group containing up to about 18 carbon atoms, an ester group containing up to about 8 carbon atoms, an ether group containing up to about 8 carbon atoms, or an acyl group containing up to about 8 carbon atoms; each Z is independently selected from a divalent linear, branched or cyclic alkyl group containing from 2 to 25 carbon atoms, a divalent linear, branched or cyclic alkenyl group containing from 2 to 25 carbon atoms, and a divalent unsubstituted or substituted aryl group of up to about 20 carbon atoms; each M is independently hydrogen, a hydroxy group, an alkenyl group of from 2 to about 12 carbon atoms, an alkynyl group of from 2 to about 12 carbon atoms, an amino group, an alkoxy group containing from 1 to about 8 carbon atoms, an alkoxyalkyl group containing from 2 to about 10 carbon atoms, an oximoalkyl group containing up to about 8 carbon atoms, wherein the lower endpoint can be 1, 2 or 3, an enoxyalkyl group containing up to about 8 carbon atoms, wherein the lower endpoint can be 1, or 2, an aminoalkyl group containing up to about 8 carbon atoms, wherein the lower endpoint can be 1 or 2, a carboxyalkyl group containing up to about 8 carbon atoms wherein the lower endpoint can be 1 or 2, an amidoaliphatic group containing up to about 8 carbon atoms wherein the lower endpoint can be 1 or 2, an amidoaryl group containing up to about 12 carbon atoms wherein the lower endpoint can be 6 or 7, a carbamato alkyl group containing up to about 8 carbon atoms wherein the lower endpoint can be 2 or 3, an epoxy group containing at least 2 and up to 8 carbon atoms, an anhydride group containing at least 3 or 4 carbon atoms and up to 12 carbon atoms, a carboxyl group containing from 1 up to about 8 carbon atoms, a carbonyl group, an acyl group containing from 1 up to about 8 carbon atoms, an amide group, an ionic group, an imine group containing from 1 or 2 up to about 8 carbon atoms, an isocyanate group, a nitrile group, an (meth)acryl group, an (meth)acrylol group, an alkoxysilyl group containing from 1 to about 8 carbon atoms, an alkoxyalkylsilyl group containing from 2 to about 8 carbon atoms, an acyloxysilyl group containing from 1 to about 8 carbon atoms, a hydroxyalkylsilyl group containing from 1 to about 8 carbon atoms or a thiol group; and the subscript x is an integer of from 1 to 250, the subscript y is from 0 to 100, the subscript n' is an integer greater than 1, and the subscript m is an integer of from to 1 to 5.

In yet another embodiment herein there is provided a curable composition comprising (a) a polysiloxane of the general formula (I) as described above, where M is an

$$M + R^{4} \xrightarrow{R^{1}} G = \begin{bmatrix} R^{2} \\ I \\ R^{1} \end{bmatrix} = \begin{bmatrix} R^{3} \\ I \\ R^{2} \end{bmatrix} = \begin{bmatrix} R^{3} \\ I \\ R^{3} \end{bmatrix} = \begin{bmatrix} R^{1} \\ I \\ R^{3} \end{bmatrix} = \begin{bmatrix} R^{1} \\ I \\ R^{2} \end{bmatrix} = \begin{bmatrix} R^{2} \\ I \\ R^{3} \end{bmatrix} = \begin{bmatrix} R^{3} \\ I \\ R^{4} \end{bmatrix} = \begin{bmatrix} R^{4} \\ I \\ R^{4} \end{bmatrix} = \begin{bmatrix} R^{$$

wherein each of R¹, R² and R³ is independently a linear or branched aliphatic group containing up to about 20 carbon atoms, e.g., from 1 to about 20 carbon atoms, more specifically from 2 to about 16 carbon atoms, an unsubstituted or 60 substituted aryl group containing from 6 to about 18 carbon atoms, optionally containing at least one heteroatom, and an alicyclic group containing up to about 20 carbon atoms; each R⁴ is independently a divalent alkyl group of from 1 to about 6 carbon atoms, an unsubstituted or substituted aryl group 65 containing up to about 18 carbon atoms, an unsubstituted or substituted alicyclic group containing up to about 18 carbon

alkenyl or alkynyl group, and (b) a polysiloxane of the general formula (II):

$$\begin{array}{c|c}
R^{1} & R^{2} \\
R^{5} - Si - O \\
R^{1} & R^{2} \\
R^{1} & R^{2}
\end{array}$$

$$\begin{array}{c|c}
R^{2} & R^{3} \\
Si - O \\
R^{1} & R^{5}
\end{array}$$

$$\begin{array}{c|c}
R^{1} & R^{5} \\
R^{1} & R^{2}
\end{array}$$

$$\begin{array}{c|c}
R^{1} & R^{5} \\
R^{1} & R^{2}
\end{array}$$

wherein each of R¹, R², R³, x and y is as defined above, R⁵ is hydrogen, an alkyl group of from 1 to 4 carbon atoms or phenyl, with the proviso that when y is 0 or 1, R⁵ is hydrogen.

In yet even another embodiment herein there is provided 5 a curable composition comprising (a) a polysiloxane of the general formula (I) wherein each of R¹, R², R³, R⁴, Z, x, y, and m is as defined above, and each M is independently selected from an alkenyl group, an alkynyl group, an amino group, an alkoxy group, an alkoxyalkyl, an oximoalkyl, an enoxyalkyl, an aminoalkyl, a carboxyalkyl, an aminoalkyl, an amidoaryl, a carbamatoalkyl, an epoxy group, an anhydride group, a carboxyl group, a carbonyl group, an acyl group, an amide group, an ionic group, an amide group, an ₁₅ imine group, an isocyanate, nitrile, an acryl group, an acrylol group or a thiol group, wherein these groups have the ranges of carbon atoms defined elsewhere herein, and n' is greater than 1, and (b) an initiator for photo-curing and optionally (c) a further reactive component selected from the group 20 consisting of a photo curable reactive component, a crosslinker of silane type, a filler, adhesion promoter, solvent, cure promoter, a cure retardant and combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to reactive polysiloxane compounds. Such polysiloxane compounds can be used to make copolymers therefrom, e.g., polycarbonate-polysilox-30 ane copolymers, or curable compositions with improved physical and chemical properties. The polysiloxane compounds and copolymers herein have been found to have a higher degree of polymerization which provides for improved physical properties in the resultant polymer composition. Some non-limiting examples of such improvements can be any one or more of thermal stability, high heat distortion temperature, comparative tracking index, flame resistance, refractive index, low temperature impact, flexibility without compromising transparency, low-melt viscosity, oxygen barrier property, UV resistance and adhesion, e.g., improved paintability.

Other than in the working examples or where otherwise indicated, all numbers expressing amounts of materials, reaction conditions, time durations, quantified properties of 45 materials, and so forth, stated in the specification and claims are to be understood as being modified in all instances by the term "about" whether or not the term "about" is used in the expression.

It will be understood that any numerical range recited 50 herein includes all sub-ranges within that range and any combination of the various endpoints of such ranges or sub-ranges, be it described in the examples or anywhere else in the specification.

It will also be understood herein that any of the components of the invention herein as they are described by any specific genus or species detailed in the examples section of the specification, can be used in one embodiment to define an alternative respective definition of any endpoint of a range elsewhere described in the specification with regard to that component, and can thus, in one non-limiting embodiment, be used to supplant such a range endpoint, elsewhere described.

It will be further understood that any compound, material or substance which is expressly or implicitly disclosed in the 65 specification and/or recited in a claim as belonging to a group of structurally, compositionally and/or functionally

4

related compounds, materials or substances includes individual representatives of the group and all combinations thereof.

Reference is made to substances, components, or ingredients in existence at the time just before first contacted, formed in situ, blended, or mixed with one or more other substances, components, or ingredients in accordance with the present disclosure. A substance, component or ingredient identified as a reaction product, resulting mixture, or the like may gain an identity, property, or character through a chemical reaction or transformation during the course of contacting, in situ formation, blending, or mixing operation if conducted in accordance with this disclosure with the application of common sense and the ordinary skill of one in the relevant art (e.g., chemist). The transformation of chemical reactants or starting materials to chemical products or final materials is a continually evolving process, independent of the speed at which it occurs. Accordingly, as such a transformative process is in progress there may be a mix of starting and final materials, as well as intermediate species that may be, depending on their kinetic lifetime, easy or difficult to detect with current analytical techniques known to those of ordinary skill in the art.

Reactants and components referred to by chemical name or formula in the specification or claims hereof, whether referred to in the singular or plural, may be identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant or a solvent). Preliminary and/or transitional chemical changes, transformations, or reactions, if any, that take place in the resulting mixture, solution, or reaction medium may be identified as intermediate species, master batches, and the like, and may have utility distinct from the utility of the reaction product or final material. Other subsequent changes, transformations, or reactions may result from bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. In these other subsequent changes, transformations, or reactions the reactants, ingredients, or the components to be brought together may identify or indicate the reaction product or final material.

In one embodiment herein in general formula (I) as described above (and as used elsewhere herein) each of R¹, R² and R³ are independently a linear or branched aliphatic group containing up to about 20 carbon atoms, more specifically up to about 12 carbon atoms, more specifically up to about 8 carbon atoms, wherein in one more specific embodiment the lower endpoint of such ranges can be any one of 1, 2, 3, 4 or 5, in some embodiments the branched aliphatic group can be an unsaturated group of the aforestated carbon atom lengths, or a branched hydrocarbon radical of the aforestated carbon atom lengths; an unsubstituted or substituted aryl group containing from 6 to about 18 carbon atoms, more specifically from about 6 to about 12 carbon atoms, and most specifically from 6 to about 10 carbon atoms, optionally containing at least one heteroatom, e.g., O, N or S, and in some embodiments the aryl group can be a bridged cyclic aryl group of the aforestated carbon atom lengths; and an alicyclic group containing up to about 20 carbon atoms more specifically up to about 12 carbon atoms,

more specifically up to about 8 carbon atoms, wherein in one more specific embodiment the lower endpoint of such ranges can be any one of 1, 2, 3, 4 or 5.

In a further embodiment, general formula (I) as described above (and as used elsewhere herein) can be defined such 5 that each R⁴ is independently, a divalent alkyl group of from 1 to about 6 carbon atoms, more specifically from 1 to about 4 carbon atoms and most specifically methyl or ethyl, and in one non-limiting embodiment from 2 to about 6 carbon atoms; an unsubstituted or substituted aryl group containing up to about 18 carbon atoms, more specifically up to about 12 carbon atoms, and most specifically up to about 10 carbon atoms, wherein the lower endpoint of such ranges can be any one of 6, 7, 8, 9 or 10; an ester group containing up to about 8 carbon atoms, more specifically up to about 6 15 carbon atoms and most specifically up to about 3 carbon atoms, wherein the lower endpoint of such ranges can be any one of 2 or 3; an ether group containing up to about 8 carbon atoms, more specifically up to about 6 carbon atoms and most specifically up to about 3 carbon atoms, wherein the 20 lower endpoint of such ranges can be any one of 2 or 3; or an acyl group containing up to about 8 carbon atoms, more specifically up to about 6 carbon atoms and most specifically up to about 3 carbon atoms, wherein the lower endpoint of such ranges can be any one of 1 or 2.

In another embodiment, general formula (I) as described above (and as used elsewhere herein) can be defined such that each Z is independently a divalent linear, branched or cyclic alkyl group containing up to 25 carbon atoms, more specifically up to about 20 carbon atoms, even more spe- 30 cifically up to about 16 carbon atoms, and yet even more specifically up to about 12 carbon atoms, and most specifically up to about 10 carbon atoms, e.g., 8 carbon atoms, wherein in one embodiment such ranges can have a lower branched or cyclic alkenyl group containing up to 25 carbon atoms, more specifically up to about 20 carbon atoms, even more specifically up to about 16 carbon atoms, and yet even more specifically up to about 12 carbon atoms, and most specifically up to about 10 carbon atoms, e.g., 8 carbon 40 atoms, wherein in one embodiment such ranges can have a lower endpoint of any one of 2, 3, 4 or 5, or a divalent unsubstituted or substituted aryl group of up to about 20 carbon atoms, more specifically up to about 18 carbon atoms and most specifically up to about 12 carbon atoms, wherein 45 the lower endpoint of such ranges can in some non-limiting embodiments be any one of 6, 7, 8, 9 or 10.

In another embodiment in general formula (I) as described above (and as used elsewhere herein) the subscript x is an integer of from 1 to 250, more specifically from about 1 to 50 about 100, even more specifically from 1 to about 50, yet even more specifically from 1 to about 25, more specifically from 1 to about 15 and most specifically from 1 to about 10. In one embodiment, the aforementioned ranges for the subscript "x" can have lower endpoints of any one of 2, 3, 55 4, or 5. In another embodiment in general formula (I) as described above (and as used elsewhere herein) the subscript y is an integer of from 0 to 40, more specifically from 1 to about 30, even more specifically from 1 to about 20, yet even more specifically from 1 to about 10 and most specifically 60 from 1 to about 8, wherein said ranges can in one embodiment, have a lower endpoint of any one of 2, 3, 4 or 5. In another embodiment the subscript m is from 1 to 5, more specifically from 1 to any one of 2, 3 or 4.

In one embodiment herein the polysiloxane of general 65 formula (I) as described above, has a degree of polymerization as defined by the subscript n' to be greater than 1, more

specifically ≥2, and most specifically ≥1.2 which is introduced between the siloxane blocks. It will be understood that these ranges of polymerization can in one non-limiting embodiment have upper endpoints of any one of 4, 5, 8, 10, 12, 15, 20, 35, 50, 75, 100, 250, 500, 1000, 2500, 5000 and 10,000. This degree of polymerization which can provide flexibility in selecting physical properties of a copolymer including the same.

In one non-limiting embodiment, each of R¹ and R² can be an alkyl of from 1 to 6 carbon atoms, more specifically 1 to 4 carbon atoms, such as the non-limiting examples of methyl and ethyl, more specifically methyl. In one embodiment each R¹ and R² are methyl. Further in some embodiments, each R³ group can be an aryl group of from 6 to 8 carbon atoms, such as the non-limiting example of phenyl. In one embodiment, each R³ group is phenyl. Further, in a more specific embodiment herein, the subscript x can be from 15 to 30, more specifically from 18 to 26, and in some even more specific embodiments x can be from 19 to 25, such as the non-limiting examples of 20, 22 and 24. In some embodiments, y can either be 0 or 4. In a more specific embodiment herein the definition of Z can be a divalent alkylene group of from 6 to 10 carbon atoms, more specifically from 7 to 9 carbon atoms, such as the non-limiting 25 example of wherein Z is a divalent octylene group.

It will be understood herein that in one non-limiting embodiment, any definition of any one or more of R¹, R², R³, R⁴, Z, M, x, y, n' and m can also have the same definition in any formulae that appear herein that contain such variables or subscripts.

As used herein the terminology "hydrocarbon radical" includes acyclic hydrocarbon radicals, alicyclic hydrocarbon radicals and aromatic hydrocarbon radicals.

As used herein in reference to a hydrocarbon radical, the endpoint of any one of 1, 2, 3, 4 or 5; a divalent linear, 35 term "monovalent" means that the radical is capable of forming one covalent bond per radical, the term "divalent" means that the radical is capable of forming two covalent bonds per radical and the term "trivalent" means that the radical is capable of forming three covalent bonds per radical. Generally, a monovalent radical can be represented as having been derived from a saturated hydrocarbon compound by conceptual removal of one hydrogen atom from the compound, a divalent radical can be represented as having been derived from a saturated hydrocarbon compound by conceptual removal of two hydrogen atoms from the compound and a trivalent radical can be represented as having been derived from a saturated hydrocarbon compound by conceptual removal of three hydrogen atoms from the compound. For example, an ethyl radical, that is, a —CH₂CH₃ radical, is a monovalent radical; a dimethylene radical, that is, a $-(CH_2)_2$ -radical, is a divalent radical and an ethanetriyl radical, that is, $(-)_2$ CHCH₂-radical, is a trivalent radical, each of which can be represented as having been derived by conceptual removal of one or more hydrogen atoms from the saturated hydrocarbon ethane.

As used herein, the terminology "acyclic hydrocarbon radical" means a straight chain or branched hydrocarbon radical, preferably containing from 1 to 60 carbon atoms per radical, which may be saturated or unsaturated and which may be optionally substituted or interrupted with one or more atoms or functional groups, such as, for example, carboxyl, cyano, hydroxy, halo and oxy. Suitable monovalent acyclic hydrocarbon radicals may include, for example, alkyl, alkenyl, alkynyl, hydroxyalkyl, cyanoalkyl, carboxyalkyl, alkyloxy, oxaalkyl, alkylcarbonyloxaalkylene, carboxamide and haloalkyl, such as, for example, methyl, ethyl, sec-butyl, tert-butyl, octyl, decyl, dodecyl, cetyl, stearyl,

ethenyl, propenyl, butynyl, hydroxypropyl, cyanoethyl, butoxy, 2,5,8-trioxadecanyl, carboxymethyl, chloromethyl and 3,3,3-fluoropropyl.

Suitable divalent acyclic hydrocarbon radicals include, for example, linear or branched alkylene radicals, such as, 5 for example, methylene, dimethylene, trimethylene, decamethylene, ethylene, 2-methyltrimethylene, 2,2-dimethylene and linear or branched oxalkylene radicals such as, for example, methyleneoxypropylene.

Suitable trivalent acyclic hydrocarbon radicals include, 10 for example, alkanetriyl radicals, such as, for example, 1,1,2-ethanetriyl, 1,2,4-butanetriyl, 1,2,8-octanetriyl, 1,2,4-cyclohexanetriyl and oxaalkanetriyl radicals such as, for example, 1,2,6-triyl-4-oxahexane.

As used herein the term "alkyl" means a saturated straight or branched monovalent hydrocarbon radical. In a preferred embodiment, monovalent alkyl groups are selected from linear or branched alkyl groups containing from 1 to 60 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, 20 pentyl, hexyl, heptyl, decyl, dodecyl.

As used herein the term "alkenyl" means a straight or branched monovalent terminally unsaturated hydrocarbon radical, preferably containing from 2 to 10 carbon atoms per radical, such as, for example, ethenyl, 2-propenyl, 3-butenyl, 25 5-hexenyl, 7-octenyl and ethenylphenyl.

As used herein, the terminology "alicyclic hydrocarbon radical" means a radical containing one or more saturated hydrocarbon rings, specifically containing from 4 to 12 carbon atoms per ring, per radical which may optionally be 30 substituted on one or more of the rings with one or more alkyl radicals, each preferably containing from 2 to 6 carbon atoms per alkyl radical, halo radicals or other functional groups and which, in the case of a monovalent alicyclic hydrocarbon radical containing two or more rings, may be 35 fused rings. Suitable monovalent alicyclic hydrocarbon radicals include, for example, cyclohexyl and cyclooctyl. Suitable divalent hydrocarbon radicals include, saturated or unsaturated divalent monocyclic hydrocarbon radicals, such as, for example, 1,4-cyclohexylene. Suitable trivalent alicy- 40 clic hydrocarbon radicals include, for example, cycloalkanetriyl radicals such as, for example, 1-dimethylene-2,4-1-methylethylene-3-methyl-3,4cyclohexylene, cyclohexylene.

As used herein, the terminology "aromatic hydrocarbon 45" radical" means a hydrocarbon radical containing one or more aromatic rings per radical, which may, optionally, be substituted on the aromatic rings with one or more alkyl radicals, each preferably containing from 2 to 6 carbon atoms per alkyl radical, halo radicals or other functional 50 groups and which, in the case of a monovalent aromatic hydrocarbon radical containing two or more rings, may be fused rings. Suitable monovalent aromatic hydrocarbon radicals include, for example, phenyl, tolyl, 2,4,6-trimethylphenyl, 1,2-isopropylmethylphenyl, 1-pentalenyl, naph- 55 thyl, anthryl, eugenol and allylphenol as well as aralkyl radicals such as, for example, 2-phenylethyl. Suitable divalent aromatic hydrocarbon radicals include, for example, divalent monocyclic arenes such as, for example, 1,2-phenylene, 1,4-phenylene, 4-methyl-1,2-phenylene, phenylm- 60 ethylene. Suitable trivalent aromatic hydrocarbon radicals include, for example, trivalent monocyclic arenes such as, for example, 1-trimethylene-3,5-phenylene.

In an embodiment, the present invention relates to a curable polysiloxane composition. The curable polysiloxane 65 composition provides elastomers, sealants, adhesives and coatings for desired properties and applications.

8

In one non-limiting embodiment herein the polysiloxane compound of the general formula (I) as described herein can be made by step-growth polymerization. For example, there is provided in one embodiment a method which comprises hydrosilylating a hydride-terminated polysiloxane, such as a hydride-terminated polysiloxane represented by the general structural formula (III):

wherein each R¹, R² and R³, x and y are as defined herein, with a diene or an alkyne. The diene in one embodiment can comprise a diene which contains a linear, branched or cyclic alkyl group containing from 2 to 25 carbon atoms, or more specifically any of the ranges of carbon atoms provided herein for the divalent alkyl group of the variable Z. Alternatively, the diene can contain a linear, branched or cyclic alkenyl group of from 2 to 25 carbon atoms, or more specifically any of the ranges of carbon atoms provided herein for the divalent alkenyl group of the variable Z.

This hydrosilylating of formula (III) with diene can be done under conventional hydrosilylation conditions, such as with the use of a precious metal catalyst, e.g., a platinum catalyst, and in some non-limiting embodiments can be conducted at a temperature of from 80° C. to about 110° C. and for a period of from about 5 to about 8 hours.

Many types of precious metal catalysts, e.g., platinum catalysts, are known and such platinum catalysts may be used for the hydrosilylation reaction in the present invention. When optical clarity is required the preferred platinum catalysts are those platinum compound catalysts that are soluble in the reaction mixture. The platinum compound can be selected from those having the formula (PtCl₂Olefin) and H(PtCl₃Olefin) as described in U.S. Pat. No. 3,159,601, which is hereby incorporated by reference in its entirety. A further platinum containing material usable in the compositions of the present invention is the cyclopropane complex of platinum chloride described in U.S. Pat. No. 3,159,662 hereby incorporated by reference in its entirety. Further the platinum containing material can be a complex formed from chloroplatinic acid with up to 2 moles per gram of platinum of a member selected from the class consisting of alcohols, ethers, aldehydes and mixtures of the above as described in U.S. Pat. No. 3,220,972 hereby incorporated by reference in its entirety. The catalysts most specifically used herein are described in U.S. Pat. Nos. 3,715,334; 3,775,452; and U.S. Pat. No. 3,814,730 to Karstedt the contents of which are incorporated by reference herein in their entireties. Additional background concerning the art may be found at J. L. Spier, "Homogeneous Catalysis of Hydrosilation by Transition Metals, in Advances in Organometallic Chemistry, volume 17, pages 407 through 447, F. G. A. Stone and R. West editors, published by the Academic Press (New York, 1979), the contents of which is incorporated by reference in its entirety.

In one embodiment the precious metal catalysts that may be used herein, are such as the non-limiting examples of rhodium, ruthenium, palladium, osmium, iridium and platinum catalysts and combinations thereof.

In one embodiment herein the platinum catalyst is in a soluble complex form.

In one other embodiment, the platinum catalyst is selected from the group consisting of platinic chloride, chloroplatinic acid, bis(acetylacetonato)platinum, (η^5 -cyclopentadienyl) trialkylplatinum and combinations thereof.

Persons skilled in the art can easily determine an effective 5 amount of precious metal catalyst. The catalyst can be present in a very wide range, but normally a range of from about 0.1 to about 10,000 ppm, more specifically of from about 1 to about 100 ppm.

The method of hydrosilylating of formula (III) with diene 10 can provide a hydride-terminated polysiloxane represented by the structural formula (IV):

acetate, allyl acetoacetate, allyl alcohol, allyl alcohol propoxylate, allyl amine, allyl amine hydrochloride, allyl benzyl ether, allyl butyl ether, allyl butyrate, allyl cyanide, allyl chloroacetate, allyl cyclohexane propionate, allyl methyl carbamate, allyl methyl carbonate, allyl methylsulfone, 2-allyloxybenzaldehyde, allyloxyethanol, 4-allyloxy-2-hydroxybenzophenone, 3-allyloxy-2-hydroxy-1-propane-sulfonic acid sodium salt, 3-allyloxy-1,2-propanediol, allyl phenyl ether, allylphosphonic acid, allyl sulfonic acid, allyl propyl

ether, allyl trifluoroacetate, tert-butyl N-allyl carbamate,

trimethylolpropane allyl ether, vinyl acetate, vinyl benzoate,

$$H \xrightarrow{R^{1}} O \xrightarrow{R^{2}} O \xrightarrow{Si} O \xrightarrow{Si} O \xrightarrow{Si} O \xrightarrow{Si} O \xrightarrow{R^{1}} \begin{bmatrix} R^{2} & R^{1} & R^{2} & R^{3} & R^{1} \\ R^{1} & R^{2} & R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} H$$

$$= \begin{bmatrix} R^{2} & R^{3} & R^{3} & R^{3} & R^{3} \\ R^{2} & R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R^{3} \\ R^{3} & R^{3} & R^{3} \end{bmatrix}_{y} \xrightarrow{R^{1}} \begin{bmatrix} R^{3} & R^{3} & R$$

wherein each of R¹, R², R³, Z, x, y and n' are as defined. In one embodiment, the method can then further comprise hydrosilylation of the hydride-terminated polysiloxane of formula (IV) with an unsaturated compound of the general formula (V):

$$[R^{4*} \frac{1}{m} M]$$
 (V)

where R^{4*} is selected from an alkenyl group containing from 2 to 6 carbon atoms, more specifically 2 to 4 carbon atoms, such as an allyl group or a vinyl group, allyl acyl group containing up to 15 carbon atoms, a vinyl acyl group containing up to 15 carbon atoms, allyl carbonyloxy group of up to 15 carbon atoms, allyl phenyl group of up to about 18 carbon atoms, vinyl phenyl group of from 8 to about 18 carbon atoms, allyl ether group of up to 8 carbon atoms, 40 vinyl ether group of up to S carbon atoms, wherein one or more of such R^{4*} groups can optionally contain one or more of a hydroxyl group, an alkoxy group of from 1 to 4 carbon atoms, a hetero atom such as O, N or S; M is as defined above for formula (I), and the subscript in is an integer of 45 from 1 to 5 and as described herein, and when the subscript m=1, then the aforementioned groups of R^{4*} are terminal groups, and when the subscript m is >1 then the aforementioned groups of R^{4*} comprise at least one divalent group and one terminal group, to obtain the polysiloxane com- 50 pound of formula (I). Some non-limiting examples of the compound of the general formula (V) include eugenol, allyl

vinyl alcohol, vinyl amine, vinyl acetoacetate, vinyl 4-tertise butylbenzoate, vinyl chloroformate, vinyl chloroformate, vinyl chloroformate, vinyl neononanoate, vinyl decanoate, vinyl neononanoate, vinyl propionate, vinyl stearate, vinyl trifluoroacetate, vinyl valerate, p-vinyl phenol, o-vinyl phenol, p-allyl phenol, o-allyl phenol, vinyl cyanate, vinyl thiocyanate, styrene, α-methylstyrene, allylphenol, vinylphenylamine, allylphenylamine, monomers of vinylnitro, vinyl acetic, vinylcarboxy, vinylbenzoate, vinylphenylsulfides, allyl(meth)acrylate, isocyanates, thiocyanates and mixtures thereof. Such hydrosilylation can occur at the same conditions as described above.

In one non-limiting embodiment, instead of hydrosily-lation, the polysiloxane of the general formula (I) can also be prepared by any one or more of anionic polymerization, free-radical polymerization, ring-opening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET), and coordination polymerization, which polysiloxane of the general formula (I) can also use as structural unit in the copolymer described herein.

In one non-limiting embodiment herein there is provided a method for the preparation of the reactive polysiloxane of formula (I) which is depicted by the reaction scheme:

Step Growth Polymerization Hydrosilylation catalyst

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ &$$

wherein R^1 , R^2 , R^3 , R^4 , R^{4*} , M, Z, m, n', x and y are defined 20 above and Z' is a chemical bond or a divalent linear, branched or cyclic alkyl groups containing up to 16 carbon atoms.

can be conducted under the conditions described above.

In one embodiment herein in the method described for making the polysiloxane (I) after the hydrosilylation of the compound of formula (IV) with the compound of formula (V), the method can further comprise purifying the siloxane $_{30}$ of the formula (I) from the reaction product mixture. Any conventional method of purification can be used, such as filtration, extraction, distillation and the like. Some more specific methods of purifying the reaction product mixture vapor-liquid separation, a packed bed column distillation, a rotary thin film evaporation and an evaporator-stripper purification.

The polysiloxane compounds of general formula (I) have improved properties over that of conventional polysiloxane 40 compounds that are used in polymer compositions, e.g., polycarbonate compositions, such as polysiloxanes which do not have one or more polymerized alkyl, alkenyl or aryl spacers in the molecule. In one non-limiting embodiment the polysiloxane of general formula (I) can have an improve- 45 ment over such other siloxanes in an improvement in at least one of refractive index, temperature of decomposition, high molecular weight, lower polydispersity, unimodal distribution and glass transition temperature.

In one embodiment, the polysiloxane of general formula 50 (I) can have one or more of a refractive index of from 1.40 to about 2.25, more specifically from about 1.42 to about 1.98; a temperature of decomposition of from about 350 to about 520° C. and more specifically from about 375 to about 500° C.; a high molecular weight of from about 3.5 to about 55 12 kDa more specifically from about 4.0 to about 10.0 kDa, said molecular weights being weight average molecular weight; lower polydispersity of from about 1.10 to about 3.0, more specifically from about 1.20 to about 2.5, and a glass transition temperature of from about -60 to about -130. In 60 one embodiment, the weight average molecular weight is determined in accordance with ASTM D5296-11, Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by high Performance Size-Exclusion Chromatography.

In one embodiment herein there is provided a curable composition comprising at least one polysiloxane of the

general formula (I) as described herein. In one further embodiment, such a curable composition comprising at least one polysiloxane of the general formula (I) can further comprise a polysiloxane of the general formula (II) as The hydrosilylation steps in the above reaction scheme ₂₅ described herein, and/or a crosslinker or chain extender. In one embodiment, the crosslinker or chain extender is a silane or siloxane crosslinker or chain extender. In one more specific embodiment, the silane or siloxane crosslinker or chain extender is selected from an alkoxysilane, an alkoxysiloxane, an oximosilane, an oximosiloxane, an enoxysilane, an enoxysiloxane, an aminosilane, a carboxysilane, a carboxysiloxane, an alkylamidosilane, an alkylamidosiloxane, an arylamidosilane, an arylamidosiloxane, an alkoxyaminosilane, an alkaryaminosiloxane, an alkoxycarcan comprise thin film evaporation, pre-evaporation, a 35 bamatosilane, an alkoxycarbamatosiloxane, and combinations of two or more thereof.

> According to one embodiment, the crosslinker component is chosen from tetraethylorthosilicate (TEOS); methyltrimethoxysilane (MTMS); vinyltrimethoxysilane; methylvinyldimethoxysilane; dimethyldimethoxysilane; dimethyldiethoxysilane; vinyltriethoxysilane; tetra(n-propyl) orthosilicate; tris(methylethylketoximo)vinylsilane; tris (methylethylketoximo)methylsilane; tris(acetamido) bis(acetamido)dimethylsilane; methylsilane; tris(Nmethylacetamido)methylsilane; bis(N-methylacetamido) dimethylsilane; (N-methylacetamido)methyldialkoxysilane; tris(benzamido)methylsilane; tris(propenoxy)methylsilane; alkyldialkoxyamidosilanes; alkylalkoxybisamidosilanes; methylethoxybis(N-methylbenzamido)silane; methylethoxydibenzamidosilane; methyldimethoxy(ethylmethylketoximo)silane; bis(ethylmethylketoximo)methylmethox-(acetaldoximo)methyldimethoxysilane; ysilane; (N-methylcarbamato)methyldimethoxysilane; (N-methylcarbamato) ethyldimethoxy silane; (isopropenoxy)methyldimethoxysilane; (isopropenoxy)trimethoxysilane; tris(isopropenoxy)methylsilane; (but-2-en-2-oxy) methyldimethoxysilane; (1-phenylethenoxy) methyldimethoxysilane; 2-((1-carboethoxy)propenoxy) bis(N-methylamino)methylmethyldimethoxysilane; methoxysilane; (N-methylamino)vinyldimethoxysilane; tetrakis(N,N-diethylamino)silane; methyldimethoxy(N-methylamino)silane; methyltris(cyclohexylamino)silane; methyldimethoxy(N-ethylamino)silane; dimethylbis(N,Ndimethylamino)silane; methyldimethoxy(N-isopropy-65 lamino)silane dimethylbis(N,N-diethylamino)silane; ethyldimethoxy(N-ethylpropionamido)silane; methyldimethoxy (N-methylacetamido)silane; methyltris(N-

methylacetamido)silane; ethyldimethoxy(Nmethyltris(N-methylbenzamido) methylacetamido)silane; silane; methylmethoxybis(N-methylacetamido)silane, methyldimethoxy(s-caprolactamo)silane; trimethoxy(Nmethylacetamido)silane; methyldimethoxy(O-ethylacetimidato)silane; methyldimethoxy(O-propylacetimidato)silane; methyldimethoxy(N,N',N'-trimethylureido)silane; methyldimethoxy(N-allyl-N',N'-dimethylureido)silane; methyldimethoxy(N-phenyl-N',N'-dimethylureido)silane; methyldimethoxy(isocyanato)silane; dimethoxydiisocyanatosilane; 10 methyldimethoxy-isothiocyanatosilane; methylmethoxydiisothiocyanatosilane; methyltriacetoxysilane; methylmethoxydiacetoxysilane; methylethoxydiacetoxysilane; methylisopropoxydiacetoxysilane; methyl(n-propoxy)diacetoxysilane; methyldimethoxyacetoxysilane; methyldi- 15 methyldiisopropoxyacetoxysilane; ethoxyacetoxysilane; methyldi(n-propoxy)acetoxysilane; or the condensates thereof; or a combination of two or more thereof.

In one non-limiting embodiment, there is provided herein a curable composition comprising at least one polysiloxane 20 of the general formula (I) as described herein, and a polysiloxane of the general formula (II) as described herein, wherein each of R¹, R², R³, R⁴, x, y, and m in formula (H) is as defined in formula (I) herein, and both M groups in formula (I) are alkenyl groups of from 2 to about 12 carbon 25 atoms. Such as the non-limiting example of where both M groups in formula (I) are an alkenyl of from 2 to about 12 carbon atoms. It is embodied herein that the M groups in formula (I), when alkenyl, can be the same or different alkenyl group of from 2 to about 12 carbon atoms. Such 30 curable compositions as described herein can further comprise at least one of a catalyst, adhesion promoter, filler, cure promoter and solvent as described herein. In one nonlimiting embodiment formula (I) can be as described herein wherein each M is a hydroxy group and wherein the adhe- 35 sion promoter is as described herein.

In one more specific embodiment, the curable composition comprising at least one polysiloxane of the general formula (I) can further comprise a cure catalyst and/or initiator. In one embodiment, the cure catalyst is selected 40 from the group consisting of metal, metal chelate, an amine, an acid, a base, and combinations thereof.

In yet one more specific embodiment, the curable composition comprising at least one polysiloxane of the general formula (I) can further comprise an optional component 45 selected from the group consisting of an adhesion promoter; filler and, mixtures thereof. Some non-limiting examples of adhesion promoter can be such that comprise an amino group containing silane or a mixture of different amino group containing silanes. The amino group-containing silane 50 adhesion promoter agent is a compound having a group containing a silicon atom bonded to a hydrolyzable group (hereinafter referred to as a hydrolyzable group attached to the silicon atom) and an amino group. Specific examples thereof include the same silyl groups with hydrolyzable 55 groups described above. Among these groups, the methoxy group and ethoxy group are particularly suitable. The number of the hydrolyzable groups may be 2 or more, and particularly suitable are compounds having 3 or more hydrolyzable groups.

Some non-limiting examples of suitable adhesion promoters include, N-(2-aminoethyl)aminopropyltrimethoxysilane gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, bis(gamma-trimethoxysilylpropyl)amine, N-phenyl-gamma-aminopropyltrimethoxysilane, triamino- 65 functionaltrimethoxysilane, gamma-aminopropylmethyl-dimethoxysilane, gamma-aminopropylmethyldiethoxysi-

14

methacryloxypropyltrimethoxysilane, lane, methylaminopropyltrimethoxysilane, gamma-glycidoxypropylethyldimethoxysilane, gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxyethyltrimethoxysilane, gamma-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, beta-(3,4-epoxycyclohexyl)ethylmethyl-dimethoxysilane, epoxylimonyltrimethoxysilane, isocyanatopropyltriethoxysilane, isocyanatopropyltrimethoxysilane, isocyanatopropylmethbeta-cyano-ethyl-trimethoxysilane, yldimethoxysilane, gamma-acryloxypropyl-trimethoxy-silane, gamma-methacryloxypropyl-methyldimethoxysilane, alpha, omega-bis-(aminoalkyl-diethoxysilyl)-polydimethylsiloxanes (Pn=1alpha, omega-bis-(aminoalkyl-diethoxysilyl)-octamethyltetrasiloxane, 4-amino-3,3,-dimethyl-butyl-tri-N-ethyl-3-tri-methoxy-silyl-2methoxysilane, and 3-(diethyl-aminopropyl)methylpropanamine, trimethoxysilane combinations of two or more thereof, and the like. Particularly suitable adhesion promoters include bis(alkyltrialkoxysilyl)amines and tris(alkyltrialkoxysilyl) amines including, but not limited to, bis(3-propyltrimethoxysilyl)amine and tris(3-propyltrimethoxysilyl)amine.

Some more specific non-limiting examples of adhesion promoters can include those selected from the group consisting of aminoalkyltrialkoxysilane, aminoalkylalkyldialkoxysilane, bis(alkyl-trialkoxysilyl)amine, tris(alktrialkoxysilyl)amine, tris(alkyltrailkoxysilyl)-cyanurate, tris (alkyltrialkoxysilyl)isocyanurate, and combinations thereof.

The filler can be reinforcing or non-reinforcing fillers or combinations thereof. In one embodiment the filler is selected from the group consisting of fumed silica, precipitated silica, clay, carbon black, calcium carbonates and combinations thereof.

In another more specific embodiment, the curable composition comprising at least one polysiloxane of the general formula (I) can further comprise an optional component selected from the group consisting of UV stabilizer, antioxidant, cure accelerator, thixotropic agent, plasticizer, moisture scavenger, pigment, dye, surfactant, solvent and combinations thereof.

In one other embodiment herein, there is provided a curable composition comprising (a) a polysiloxane of the general formula (I), where each M is independently selected from an alkenyl group, an alkynyl group, an amino group, an alkoxy group, an alkoxyalkyl, an oximoalkyl, an enoxyalkyl, an aminoalkyl, a carboxyalkyl, an amidoalkyl, an amidoaryl, a carbamatoalkyl, an epoxy group, an anhydride group, a carboxyl group, a carbonyl group, an acyl group, an amide group, an ionic group, an amide group, an azo group, an imine group, an isocyanate, nitrile, nitrate, nitro, nitroso group, an acryl group, an acrylol group or a thiol group, x is from 1 to 250, y is from 0 to 100, n' is greater than 1 and m is from to 1 to 5, (b) an initiator for photo-curing and optionally, (c) a further reactive component selected from the group consisting of a photo curable reactive component, a crosslinker of silane type, a filler, adhesion promoter, solvent, cure promoter, a cure retardant and combinations thereof.

In one embodiment herein any one of the polysiloxane of the general formula (I), the copolymer thereof as described herein, the composition of copolymer and further polymer or the curable composition(s) as described herein can be used to form an article. The article can be any article that would be benefited by the improved physical and/or chemical properties described herein. Some technologies that would benefit such an article include automotive, electronic and medical technologies. In one embodiment the article can be made by molding, shaping, or forming the any one of the

polysiloxane of the general formula (I), the copolymer thereof as described herein, or the composition of copolymer and further polymer described herein to obtain the article.

In one embodiment herein there is also provided a cured composition made by the process of curing any of the 5 curable compositions described herein. Such curing can be provided by any suitable method described herein, such as for example, by addition curing, condensation curing and/or ultraviolet light curing. The cured composition can be any one of a solid, a fluid, a liquid or a gum. Such cured 10 compositions can be used in any one of an elastomer, a sealant, an adhesive, a coating and a combination thereof.

In one embodiment, the comparative tracking index is measured using ASTM D5288-14, Standard Test Method for Determining Tracking Index of Electrical Materials Using 15 Various Electrode Materials. In another embodiment, the haze is determined in accordance with ASTM D1003-13, Standard Test Method for Haze and Luminous Transmittance. In still another embodiment, the physical properties of composition containing the reactive polysiloxane of the 20 present invention are determined in accordance with ASTM D638-14, Standard Test Method for Tensile Properties of Plastics.

While the invention has been described with reference to certain embodiments, it will be understood by those skilled 25 in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing 30 from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed as the best mode contemplated for carrying out this invention but that the invention will include all embodiments falling within the scope of the appended 35 claims.

EXAMPLES

Example 1

Synthesis of Hydride End-Capped Hybrid Siloxane Polymer

condenser, dropping funnel and a mechanical stirrer under

16

polymerization, unreacted starting materials, volatile compounds and the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition of the copolymers are inferred through spectral and chromatographic.

wherein x is 35 and n' is 7.75

Example 2

Synthesis of Vinyl End-Capped Hybrid Siloxane Polymer

A 500 mL three neck round bottom flask fitted with a reflux condenser, dropping funnel and a mechanical stirrer under nitrogen environment was charged 25 mL of toluene and 1,7-octadiene (7.5 grams, 0.067 mol). To this solution 0.14 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was added. The whole set-up was kept in an oil bath with reaction temperature maintained at 70° C. Hydride endcapped siloxane (${}^{H}MD_{35}M^{H}$, 175 grams, 0.064 mol, wherein the silicone units of M^H and D contain methyl groups other than the one required H group in each M^H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased to 80° C. and the reaction was continued until all the hydride gets consumed. After completion of the hydrosilylation polymerization, unreacted starting materials, volatile com-40 pounds and the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition A 1 L three neck round bottom flask fitted with a reflux 45 of the copolymers are inferred through spectral and chromatographic.

$$\begin{array}{c|c} & \begin{array}{c} \text{CH}_3 \\ \text{C} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{Si} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{C} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{Si} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{Si} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{Si} \end{array} & \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} & \begin{array}{c} \text{CH}_3 \\ & \begin{array}{c} \text{CH}_3 \end{array} & \begin{array}{c} \text{CH}_3 \\ & \begin{array}{c} \text$$

nitrogen environment was charged 50 mL of toluene and 1,7-octadiene (13.35 grams, 0.121 mol). To this solution 0.29 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was added. The whole set-up was kept in an oil bath with reaction temperature maintained at 70° C. Hydride end- 60 capped siloxane (${}^{H}MD_{35}M^{H}$, 350 grams, 0.128 mol, wherein the silicone units of M^H and D contain methyl groups other than the one required H group in each M^H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased 65 to 80° C. and continue the reaction until all the 1,7-octadiene gets consumed. After completion of the hydrosilylation

wherein x is 23.6 and n' is 8.

Example 3

Synthesis of Methoxysilane End-Capped Hybrid Siloxane Polymer

A 500 mL three neck round bottom flask fitted with a reflux condenser, dropping funnel and a mechanical stirrer under nitrogen environment was charged 50 mL of toluene and 1,7-octadiene (6.65 grams, 0.061 mol). To this solution 0.14 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was

added. The whole set-up was kept in an oil bath with reaction temperature maintained at 70° C. Hydride end-capped siloxane (${}^{H}\text{MD}_{35}\text{M}^{H}$, 175 grams, 0.064 mol, wherein the silicone units of H and D contain methyl groups other than the one required H group in each H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased to 80° C. Once all 1,7-octadiene was consumed, vinyl trimethoxysilane (0.5 gram, 0.003 mol) in 25 mL of isopropylalcohol was added and reaction was continued until all

18

hydride is consumed. After completion of the hydrosilylation polymerization, unreacted starting materials, volatile compounds and the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition of the copolymers are inferred through spectral analysis.

$$\begin{array}{c} H_{3}CO \\ H_{3}CO \\ \end{array} \\ Si \\ C \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ H_{2} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ H_{2} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_{3} \\ Si \\ CH_{3} \\ \end{array} \\ \begin{array}{c} CH_{3} \\ Si \\ CH_$$

wherein x is 18.1 and n' is 5.75.

Example 4

Synthesis of Methacrylate End-Capped Hybrid Siloxane Polymer

A 500 mL three neck round bottom flask fitted with a ²⁵ reflux condenser, dropping funnel and a mechanical stirrer under nitrogen environment was charged 50 mL of toluene and 1,7-octadiene (6.65 grams, 0.061 mol). To this solution 0.14 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was added. The whole set-up was kept in an oil bath with 30 reaction temperature maintained at 70° C. Hydride endcapped siloxane (${}^{H}MD_{35}M^{H}$, 175 grams, 0.064 mol, wherein the silicone units of M^{H} and D contain methyl groups other than the one required H group in each M^H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased to 80° C. Once all 1,7-octadiene was consumed, allyl methacrylate (0.5 gram, 0.003 mol) in 5 mL of toluene was added and reaction was continued until all hydride is consumed. After completion of the hydrosilylation polymerization, unreacted starting materials, volatile compounds and 40 the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition of the copolymers are inferred through spectral analysis.

55

wherein x is 11.2 and n' is 2.2.

Example 5

Synthesis of Epoxy End-Capped Hybrid Siloxane Polymer

A 500 mL three neck round bottom flask fitted with a reflux condenser, dropping funnel and a mechanical stirrer under nitrogen environment was charged 50 mL of toluene and 1,7-octadiene (6.65 grams, 0.061 mol). To this solution 0.14 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was added. The whole set-up was kept in an oil bath with reaction temperature maintained at 70° C. Hydride end-capped siloxane (HMD₃₅MH, 175 grams, 0.064 mol,

20

wherein the silicone units of M^H and D contain methyl groups other than the one required H group in each M^H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased 5 to 80° C. Once all 1,7-octadiene was consumed, allyl glycidyl ether (0.4 gram, 0.003 mol) in 5 mL of toluene was added and reaction was continued until all hydride is consumed. After completion of the hydrosilylation polymeriza-

tion, unreacted starting materials, volatile compounds and the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition of the copolymers are inferred through spectral analysis.

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3$$

25

20 wherein x is 14 and n' is 3.65.

Example 6

Synthesis of Anhydride End-Capped Hybrid Siloxane Polymer

A 500 mL three neck round bottom flask fitted with a reflux condenser, dropping funnel and a mechanical stirrer under nitrogen environment was charged 50 mL of toluene and 1,7-octadiene (6.65 grams, 0.061 mol). To this solution 0.14 gram of Karstedt's catalyst (15 ppm of 2 wt % Pt) was added. The whole set-up was kept in an oil bath with reaction temperature maintained at 70° C. Hydride endcapped siloxane (${}^{H}MD_{35}M^{H}$, 175 grams, 0.064 mol, wherein the silicone units of M^H and D contain methyl groups other than the one required H group in each M^H) in a dropping funnel was added drop wise over a period of 1 hour. The reaction temperature was subsequently increased 40 to 80° C. Once all 1,7-octadiene was consumed, 5-norbornene-endo-2,3-dicarboxylic anhydride (0.55 gram, 0.003 mol) in 5 mL of toluene was added and reaction was continued until all hydride is consumed. After completion of the hydrosilylation polymerization, unreacted starting materials, volatile compounds and the solvent were stripped under reduced pressure. The final product was obtained as a yellow color liquid in quantitative yield and was decolorized with activated charcoal to yield the desired product as a colorless liquid in quantitative yield. The chemical structure and composition of the copolymers are inferred through spectral analysis.

$$\begin{array}{c|c} CH_3 & CH_3 &$$

Cure Formulations

The synthesized vinyl end-capped hybrid siloxane polymer of example 2 and the synthesized hydride end capped hybrid siloxane polymer of example 1 was independently mixed in different proportions with component A and component B of commercially available elastomer formulation of Liquid silicone rubber (LSR 2050, Momentive) respectively in a blender and were cured by compression molding at 180° C. for 10 min under pressure to get an elastomeric sheet. The respective sheets were analyzed for % transmittance, haze, yellowness index (YI) and % elongation (Table 1).

22

atoms, a divalent ester group containing up to about 8 carbon atoms, or a divalent ether group containing up to about 8 carbon atoms;

each occurrence of Z is independently selected from a divalent linear, branched or cyclic alkyl group containing from about 2 to about 25 carbon atoms, a divalent linear, branched or cyclic alkenyl group containing from about 2 to about 25 carbon atoms, and a divalent unsubstituted or substituted aryl group of up to about 20 carbon atoms;

each occurrence of M is independently a hydroxy group, an alkynyl group of from about 2 to about 12 carbon atoms, an amino group, an alkoxy group containing from about 1 to about 8 carbon atoms, an alkoxyalkyl group containing from about 2 to about 10 carbon

TABLE 1

	Comparative Example 1	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17
LSR2050	100	80	60	80	60	100	100	80	80	60	60	60
Component A vinyl		20	4 0									
substituted polysiloxane Example 2		2~		20	4 0			20	20	4 0	4 0	4 0
LSR2050	100	100	100	100	100	95	90	95	90	95	90	80
Component B Example 1						5	10	5	10	5	10	
Total	200	200	200	200	200	200	200	200	200	200	200	200
% Transmitance	90.6	90	90.5	89.9	89.7	90.1	90.3	90.1	90.1	89.4	89.3	88.9
Haze	33	8	5.6	5.02	33.4	38.7	15.4	15.7	17.7	33.1	8.51	37.7
YI	3.58	4.89	5.45	5.86	5.12	3.58	4.66	5.37	5.48	5.38	6.72	5.2
% elongation	456	489	459	49 0	481	523	544	492	464	434	414	404

LSR 2050—Liquid silicone rubber, Momentive Inc.

The invention claimed is:

1. A polysiloxane having the general structural formula (I):

$$M + R^{4} + \frac{1}{m} + \frac{1}{Si} + O + \frac{1}{Si} + O$$

wherein

each occurrence of R¹, R² and R³ is independently a linear or branched aliphatic group containing up to about 20 55 carbon atoms, an unsubstituted or substituted aryl group containing from about 6 to about 18 carbon atoms, optionally containing at least one heteroatom, and an alicyclic group containing up to about 20 carbon atoms;

each occurrence of R⁴ is independently a divalent alkyl group of from about 1 to about 6 carbon atoms, a divalent unsubstituted or substituted aryl group containing up to about 18 carbon atoms, a divalent unsubstituted or substituted alicyclic group containing up to 65 about 18 carbon atoms, a divalent unsubstituted or substituted acyl group containing up to about 18 carbon

atoms, an oximoalkyl group containing up to about 8 carbon atoms, an enoxyalkyl group containing up to about 8 carbon atoms, an aminoalkyl group containing up to about 8 carbon atoms, a carboxyalkyl group containing up to about 8 carbon atoms, an amidoaliphatic group containing up to about 8 carbon atoms, an amidoaryl group containing up to about 12 carbon atoms, a carbamato alkyl group containing up to about 8 carbon atoms, an anhydride group, a carboxyl group containing up to about 8 carbon atoms, a carbonyl group, an acyl group containing up to about 8 carbon atoms, an amide group, an ionic group, an imine group containing up to about 8 carbon atoms, an isocyanate group, a nitrile group, an (meth)acryl group, an (meth) acrylol group, an alkoxysilyl group, an alkoxyalkylsilyl group, an acyloxysilyl group, a hydroxyalkylsilyl group or a thiol group; and

the subscript x is an integer of from 1 to 250, the subscript y is an integer from 0 to 100, the subscript n' is an integer from 2 to 10,000, and the subscript m is an integer of from to 1 to 5.

2. A method of preparing the polysiloxane compound (I) of claim 1, comprising:

hydrosilylating a hydride terminated polysiloxane represented by the general structural formula (III)

each R¹, R², R³, x and y are as defined in claim 1,

with a diene which contains a linear, branched or cyclic 10 alkyl group containing from about 2 to about 25 carbon atoms or a linear, branched or cyclic alkylene group of from about 2 to about 25 carbon atoms to obtain a hydride-terminated polysiloxane represented by the structural formula (IV):

24

5. An elastomer, a sealant, an adhesive, a coating or a combination thereof comprising the curable composition of claim 3, wherein the curable composition is cured.

6. The polyslioxane of claim 1, wherein M is a hydroxy group, an aminoalkyl group containing up to about 8 carbon atoms, an anhydride group, an isocyanate group, an alkoxysilyl group, an alkoxyslkylsilyl group, an acyloxysilyl group or a thiol group.

7. The polysiloxane of claim 1, wherein n' is from 2 to 35.

8. The polysiloxane of claim 1, wherein n' is, from 2 to 4.

9. The polysiloxane of claim **1**, wherein x is from 1 to 50.

10. The polysiloxane of claim 1, wherein x is from 1 to 15.

11. The polysiloxane of claim 1, wherein x is from 15 to 30.

12. The polysiloxane of claim 1, wherein y is from 1 to 8.

$$H \xrightarrow{R^{1}} O \xrightarrow{R^{2}} O \xrightarrow{Si} O \xrightarrow{Si} O \xrightarrow{Si} V \xrightarrow{Si} O \xrightarrow{Si} V \xrightarrow{R^{1}} V \xrightarrow{R^{2}} V \xrightarrow{Si} O \xrightarrow{Si} V \xrightarrow{R^{1}} V \xrightarrow{R^{2}} V \xrightarrow{R^{1}} V \xrightarrow{R^{2}} V \xrightarrow{R^{1}} V \xrightarrow{R^{1$$

wherein each of R^1 , R^2 , R^3 , y and n' are as defined in claim 1.

followed by hydrosilylation of the hydride-terminated 35 polysiloxane of formula (IV) with an unsaturated compound of the general formula (V):

$$[R^{4*}]_m$$
 M (V) 40

wherein R^{4*} is chosen from an alkenyl group containing from about 2 to about 6 carbon atoms, an allyl acyl group 45 containing up to about 8 carbon atoms, a vinyl acyl group containing, up to about 8 carbon atoms, an allyl carbonyloxy group of up to about 8 carbon atoms, an allyl phenyl group of up to about 18 carbon atoms, a vinyl phenyl group of up to about 18 carbon atoms, an allyl ether group of up to about 8 carbon atoms, or a vinyl ether group of up to about 8 carbon atoms, wherein one or more of such R4* groups can optionally contain one or more of a hydroxyl group, an alkoxy group of from about 1 to about 4 carbon atoms, or a heteroatom; M is as defined in claim 1, and the subscript in is an integer of from 1 to 5, and wherein when the subscript $_{60}$ m=1, the R^{4*} groups are terminal groups, and when the subscript m is >1 then the R^{4*} groups comprise at least one divalent group and one terminal group.

- 3. A curable composition comprising at least one polysi- 65 loxane according to claim 1.
 - 4. An article comprising the polysiloxane of claim 1.

13. The polysiloxane of claim 1, wherein y is 0.

14. The polysiloxane of claim 1, wherein m is 1.

15. The polysiloxane of claim **1**, wherein each R¹ d R² is an alkyl of from 1 to 4 carbon atoms.

16. The polysiloxane of claim **1**, wherein each R¹ and R² is a methyl group.

17. The polysiloxane of claim 1, wherein R³ is a phenyl group.

18. The polysiloxane of claim 1, wherein Z is a divalent alkylene group from 6 to 10 carbon atoms.

19. The polysiloxane of claim 1, wherein Z is a divalent octylene.

20. The article of claim 4, wherein M is a hydroxy group, an aminoalkyl group containing up to about 8 carbon atoms, an anhydride group, an isocyanate group, an alkoxysilyl group, an alkoxyalkylsilyl group, an acyloxysilyl group or a thiol group.

21. The article of claim 4, wherein n' is from 2 to 35, x is 1 to 50 and y is 0 to 40.

22. The article of claim 4, wherein n' is from 2 to 4, x is 1 to 15 and y is 1 to 8.

23. The article of claim 4, wherein each R^1 and R^2 is a methyl group, R^3 is a phenyl group and Z is a divalent alkylene group of from 6 to 10 carbon atoms.

24. The article of claim 4, wherein m is 1.

* * * * *